Evaluation of the interface properties of recombination sensors from the measurement of capacitance-voltage characteristics

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***Abstract* — It was investigated the problem of silicon substrate selection for the sensor structure based on deep junction barrier structure. The described sensor realizes photoelectrical conversion principle for the illumination with light that has high absorption coefficient in the silicon. The method of substrate pre-selection based on the measurement of capacitance-voltage *C-V* characteristics has been proposed in the work. The evaluation of the curves allows creating the sensors with reproducible characteristics. As shape of the *C-V* curves in the system liquid analyte/silicon substrate (with or without chemically modified silicon surface) strongly depends on charge state of the interface and near-surface band bending, some recommendation for silicon substrate choosing can be done. The obtained results indicate that the shift of the saturation voltage of the *C-V* curves correlates with peculiarities of photocurrent distribution in the deep silicon barrier structure, so the effective recombination sensors with reproducible characteristic can be formed.**

Keywords—Surface recombination, chemical sensor, analyte

I. INTRODUCTION

The recombination sensor based on “deep” silicon barrier structure can be regarded as effective structure that realize photoelectrical transducer principle Fig.1 [1]. The adsorbtion of polar molecules on the illuminated surface usually changes the recombination parameters (concentration of recombination levels, their energy value, recombination centers cross sections) and pre-surface band-dending Y_s. The value of surface recombination S and pre-surface band bending Y_s are described in terms of Stevenson-Keyes theory and its modifications [2]. If the pre-surface band bending in the silicon wafer corresponds to close value of electron and hole concentration, the surface recombination has maximal value. On the other hand, the surface recombination decreases drastically in the case of lacking of electrons or holes near illuminated surface. If the illumination with high absorption coefficient used and the thickness of active layer d is chosen close to minority charge carrier diffusion length l, the photocurrent I through barrier structure depends on the surface recombination significantly [2,3]. The absorption efficiency can be increased and the interface properties can be stabilized by the formation of thin nano-textured films (organic or inorganic) on the silicon surface [4,5]. The adsorption of the polar molecules can be recognized by measurement of barrier structure photocurrent, Fig.1 [2,3]. The criterion of the sensor efficiency is the high value of relative change of photocurrent due to change of surface recombination at adsorption of analyte. The operation principle described above can be also applied for sensory system like “electronic nose” or “electronic tongue”. For example, to create such structure, the partial modification of the silicon surface by organic or nonorganic layer should be

done to realize the artificial heterogeneity [3]. Comparing with traditional structure like LAPS, recombinational sensor has more simple structure and it can be used both for liquid and gas analytes.

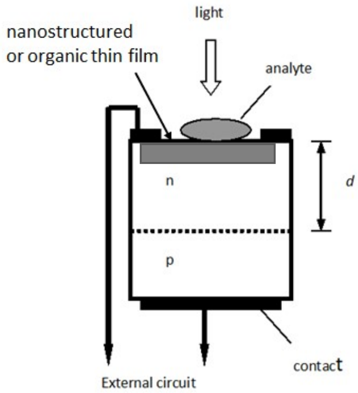


Fig. 1. Schematic image of sensor structure based on deep silicon barrier structure with nanostructured layer on the silicon surface

It should be noted that efficiency of such sensor strongly depends on the initial charge state at the surface of silicon wafer. However, the initial band bending in the silicon wafer can be different for different silicon substrate formed even in similar technological process. Since the modifications of the silicon wafer due to thin polymeric layers deposition require considerable time and material costs, it is necessary to propose a certain express method of substrate selection. In present work we consider an effective method for silicon structure selection by measurement of capacitance-voltage characteristics. The proposed method allows to select the silicon substrates for recombination sensors with similar characteristics. It can be useful for creation of recombination sensor with high *dI/dS*ratio.

II. THEORY

As it was mentioned, the recombination sensor operates usually without applying external bias. It was shown that photocurrent depends on the recombination properties of the illuminated surface in the case when the region, where non-equilibrium holes are generated ($1/\alpha(\lambda) \sim 1\mu$m), and region, where these carriers are collected by electric field, are separated in space. The photocurrent I in the deep structure significantly depends on surface recombination velocity S, it can be given as [3]:

$$i(s) \cong \frac{1+\dfrac{S}{\alpha(\lambda)D}}{s\dfrac{l}{D}sh\left(\dfrac{d}{l}\right)+ch\left(\dfrac{d}{l}\right)} \qquad (1)$$

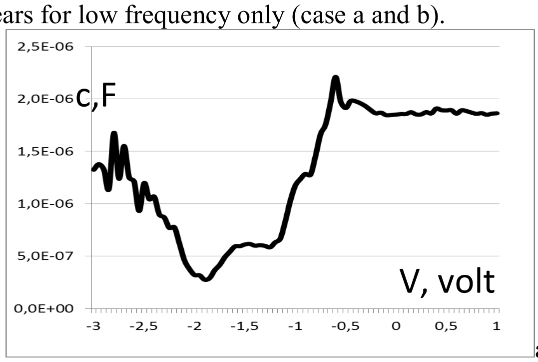
where D is minority charge carrier diffusion coefficient, $\alpha(\lambda) \sim 10^5$-$10^3$ cm^{-1}. In our case the thickness of *n-Si* wafer d is nearly 300 μm, holes diffusion length l_p is nearly 150-200 μm. The principal traits of the Stevenson-Keyes theory claim that if the concentration of non-equilibriums electrons and holes are close to each other, the S gets its maximal value, if default of electrons or holes takes place, S is strongly diminished. That is why the dependences $S(Y_s)$ typically have bell-shaped form. Thus, for optimal parameters of barrier structure, the changes of the dependences $S(Y_s)$ with polar molecule adsorption should determine the maximal changes of photocurrent.

It should be noted that direct evaluation of the recombination properties of the silicon surface represent extremely difficult problem. Some aspects that define recombination sensor efficiency can be found from the comparative analyze of the capacitance-voltage characteristics in the analyte/silicon substrate system. The peculiarities of the charge state at the interface (surface charge, character of the surface state distribution etc.) strongly correlate with the character of the dependence of the space charge region capacitance on applied bias [2,7]. Really, some features of the $S(Y_s)$ curve and consequently the possible changes of surface recombination with band bending Y_s can be predicted and evaluated from the simple analyze of *C-V* curves. These peculiarities are: 1) the inflection point of the *C-V* curves that corresponds to $d^2C/d^2V = 0$ should be closed to V=0 bias, in these case the optimal changes of pre-surface band bending Y_s can be expected; 2) the significant increase of capacitance should be observed for obtaining maximal change of photocurrent; 3) the slope of *C-V* curves should be significant for high sensitivity of recombination sensor (or, in other words, it allow receive higher value of the *dI/dS*).

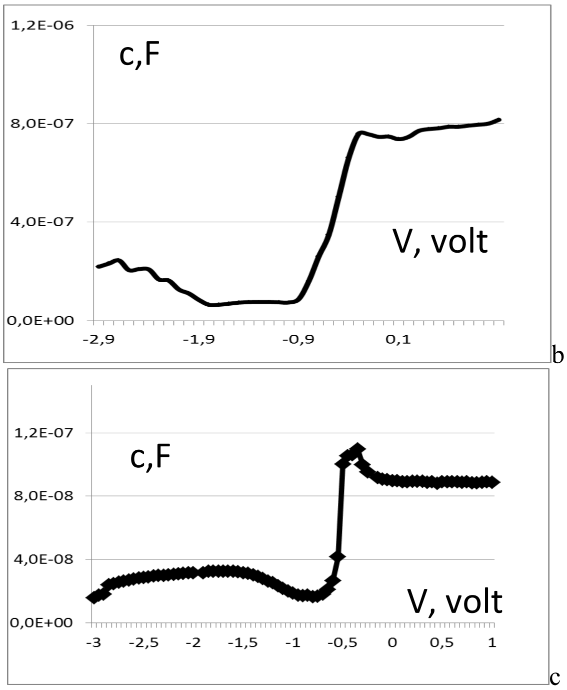
Moreover, the investigation of capacitance-voltage characteristic in the system analyte-silicon substrate can be useful also as independent and supplementing sensor structure for polar molecules detection.

III. RESULTS AND DISCUSSION

The serial SR830 Volta master conductometer was used for the capacitance-voltage measurement in the electrolyte. The silicon p-type substrate was 50 Ω*cm resistivity. The 10 nm polymeric film (fabricated from silan) was chemically deposited on silicon surface. The results of capacitance measurement for the system consisting of analyte (electrolyte with fixed pH)/p-silicon are presented in Fig 2. These curves demonstrate strong similarity to conventional characteristic of metal-insulator-semiconductor structure. It was experimentally shown that the shape of *C-V* curves does not depend on the amplitude of testing voltage (for the range 10-30 mV). Really, when the frequency of testing voltage increase (f=100 Hz, f=500 Hz, f=10000 Hz), the part of *C-V* curve corresponding to the accumulation (saturation regions) are observed for all three cases. It corresponds to positive voltage applied to p-silicon substrate. The inversion of conductivity in silicon substrate appears for low frequency only (case a and b).



a



b

c

Fig.2.The *C-V* curves received for different frequency of testing voltage *f*=100Hz (a), *f*=500Hz (b), *f*=10000Hz (c) The analyte has fixed pH=8

In other words, the generation-recombination processes of non-equilibrium carriers in silicon do not "follows" the changes of the testing voltage. This is manifested in the absence of saturation in the left branches of the presented curves. As can be seen, the low-frequency curve has some peculiarities that allows to suppose the existence of energy levels system at the interface polymeric film-silicon (case a). The absolute value of the capacitance decreases with increasing of testing signal frequency. That is why the measurement of impedance can be more beneficial for high frequency of testing signal *f*~10000Hz. It was experimentally observed that the shape of *C-V* curves rests almost unchanged for frequency in the wide range 10000-80000Hz. The character of observed physical process in the investigated system is generally defined by the charging/discharging of silicon space charge region and by the possible changing of charge state at the interface with frequency.

It was experimentally shown that if pH of the analyte changes, the shape of the *C-V* curves changes significantly. The frequency of testing signal was chosen at *f*~10000Hz. The experimental curves are demonstrated in Fig.3. As can be seen if *pH* increases from 1 to 8, the saturation region of *C-V* curve is shifted towards negative voltage. As it is well known, the higher value of *pH* corresponds to lower concentration of positive ion H^+ in the analyte. So, it can be supposed that "activity" of positive ions in the solution of the analyte changes the initial charge state of the interface and pre-surface band-bending in the silicon substrate. It means that local electric field of molecules of the analyte can influence on the local states (that can be regarded also as recombination centres) at the polymeric film/p-silicon interface. In other words, the modification of electrical parameters of the interface takes place.

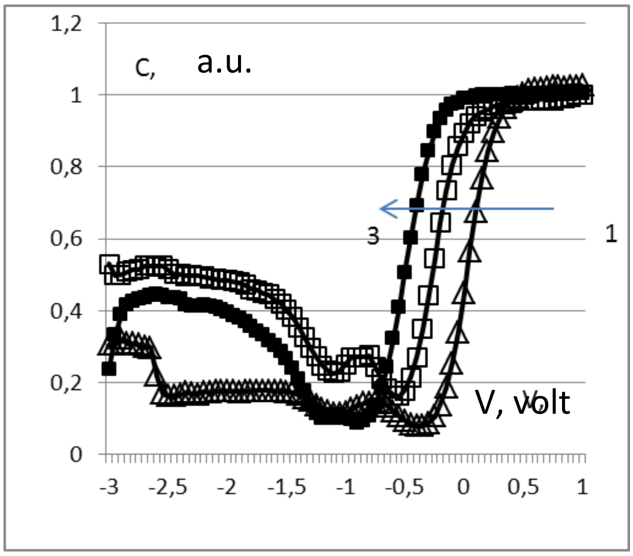


Fig.3 The high-frequency C-V curves for analytes with different pH: 1)pH=1; 2)pH=5; 3)pH=8. The silicon surface is modified with thin polymeric film

As inflection point that corresponds $d^2C/d^2V = 0$ is also shifted towards negative value of voltage with increasing of pH. It is interesting to note that slope of the *C-V* curves rests invariable for all three cases.

The peculiarities of the *C-V* curves behavior allow to use the described system for detection of the activity of positive ions in the solution. In other words, this approach can be regarded as well-known capacitance sensor for *pH* determination.

Fig.4 represents *C-V* curves for p-silicon substrate modified with thick Si_3N_4 film (the thickness of the film is about 200 nm). The frequency of testing signal was *f*~10000Hz. The "activity" of positive ions in the solution of the analyte, like the previous case, changes the initial charge state and pre-surface band-bending in the silicon substrate.

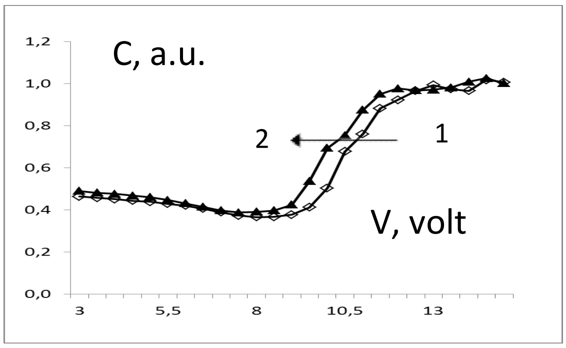


Fig.4 The high-frequency *C-V* curves for analytes with different pH 1) pH=1,2) pH=8. The silicon surface is modified with thick film Si_3N_4

Really, as can be seen, the shifting of the saturation region with *pH* takes place like in Fig.3. The slope of curves is less than for previous case. Moreover, the inflection points of the curves correspond to *V*~10 B. The bigger thickness of the Si_3N_4 film causes more significant values of positive voltage necessary to form the saturation region in silicon substrate. The comparison of the cases in Fig.3 and Fig.4 shows that direct measurement of the *C-V* curves can

provide important information on the surface state of the interface analyte/silicon..

The Fig.5 represents typical *C-V* curves experimentally observed for identical thin polymeric films on p-silicon substrates that where formed in absolutely similar technological process. As can be seen the shifting of the curves takes place in the case. It is interesting to note that the shifting of the saturation region (± 0.2 - 0.5 V) was observed with the preservation of the curve slope. It means that the initial band bending in the silicon wafer and initial charge state of the interface can be different for “identical” *p-* silicon substrates.

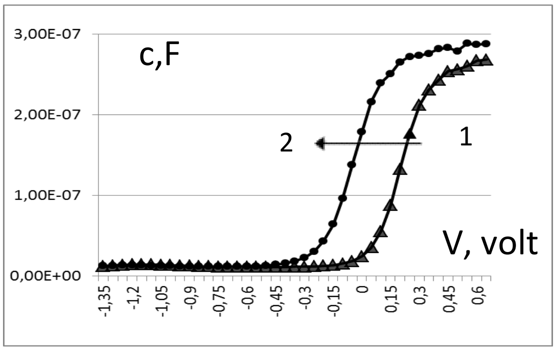


Fig.5 The high-frequency C-V curves for analytes with fixed pH =8 for two identical p-silicon substrates

The Fig. 6 a), represent typical surface distribution of photocurrent of the deep silicon barrier structure. The “identical” *p-* silicon substrates were used. The silicon surface was covered by thin films of Si_3N_4 with different properties deposed in identical conditions. The lighter points of presented distribution correspond to higher photocurrent value (i.e smaller value of the surface recombination at the interface thin film-silicon). It can be observed the difference of the photocurrent distribution appears in different way for the parts corresponding to different films.

a	b

Fig. 6 The distribution of photocurrent on the silicon substrats of p-type covered with thin. Si_3N_4 in air a) and in with water b)

The silicon surface modifed by thin films was scanned by laser beam with λ=532nm wavelength for all cases presented.

These results can be explained by different initial band bending Y_s and different recombination properties of the interface formed on silicon substrate [5-7]. As was mentioned the contact of the illuminated surface with analyte induced the changing of recombination properties [5]. Fig.6 b) represents surface distribution of photocurrent in the case of contact with water analyte. The contact with analyte leads to decreasing of photocurrent in different way for the parts corresponding to different polymeric films. That corresponds to increasing of surface recombination *S* due to changing of pre surface band-bending Y_s and changing of the recombination properties of interface.

It is clear that the stable characteristics of the interface is a principal condition for creation of effective recombination sensors with reproducible characteristics. That means that closed value of photocurrent distribution should be observed for several structures formed in identical technological process. The method described above demonstrates the possibility of substrate selection from the simple measurement of the capacitance-voltage characteristics. The evaluation of the relative shape of the *CV* curves and the relative shifting of the saturation region can be effective approach in the problem described above.

Thus, it is possible to perform the effective pre-selection of the silicon substrates (with or without polymeric film) for further surface modification.

CONCLUSION

It was shown the possibility to preselect silicon substrates for recombination sensors with reproducible characteristics. The analyze of the high frequency capacitance-voltage curves of the system analyte-silicon covered with thin polymeric film allows to evaluate the recombination properties of the interfaces in the deep barrier sensor structures. This evaluation is important aspect to create the reproducible recombination sensor of high efficiency. The principal aspects of the proposed analyze are: 1) relative shifting of saturation region of the *CV* curves should be minimal for reproducibility of the characteristic; 2) the slope of the curves should be as high as possible; 3) voltage corresponding to deflection point $d^2C/d^2V=0$ should be maximally close to zero voltage; 4) the amplitudes of the capacitance change should be maximal. The conditions 2),3),4) should provide high efficiency of recombination sensor. It was shown that polymeric film deposited from silan has greater potential for effective recombination sensor than film SI_3N_4

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